

Patent Abstracts of Japan

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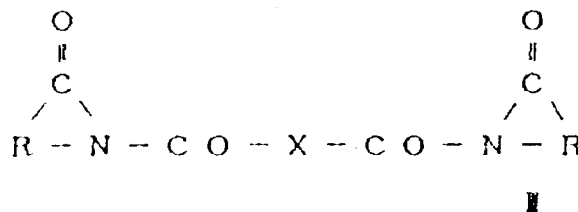
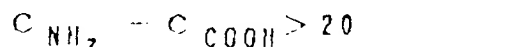
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TITLE : PREPARATION OF ULTRAHIGH  
MOLECULAR WEIGHT POLYAMIDE  
MOLDED ARTICLE



ABSTRACT : PURPOSE: To obtain an ultrahigh-MW polyamide molded article having a low lactam monomer content, small m.p. lowering and good physical properties, by melt-kneating a bifunctional N-acyllactam compd. as a chain linking agent with a specified polyamide.

CONSTITUTION: Nylon 6 satisfying formulas I and II is molded into a required shape while nylon 6 is reacted with a bifunctional N-acyllactam in a melt- kneader. As said bifunctional N-acyllactam compd., those of formula III (wherein X is an alkyl group or an atom. residue; R is an alkyl group) are used. The amt. of the bifunctional N-acyllactam added to nylon 6 is adjusted by the aimed MW and it is pref. that the amt. should be about equivalent to that of amino terminal groups of the polymer for obtaining the highest MW.

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(54) Title: METHOD FOR THE MANUFACTURE OF SUPER-HIGH-MOLECULAR-WEIGHT POLYAMIDE MOLDING

(21) Application No.: Sho 63[1988]-21349

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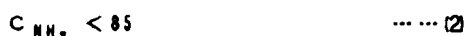
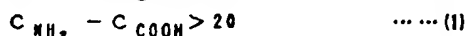
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## CLAIM

A method for the manufacture of a super-high-molecular-weight nylon 6 molding, characterized by the molding, in the desired shape, of nylon 6 of formulas (1) and (2) shown below, while being reacted with a difunctional N-acyllactam in a melt kneader:



(C<sub>NH2</sub> and C<sub>COOH</sub> respectively represent the terminal amino group and terminal carboxy group amounts in units of g-equivalents/10<sup>6</sup> g).

## DETAILED EXPLANATION OF THE INVENTION

### INDUSTRIAL APPLICATION FIELD

The present invention concerns a method for the manufacture of super-high-molecular-weight nylon 6, and more specifically concerns a method for the manufacture of moldings developing a super-high molecular weight during melt-molding. Here, "super-high-molecular weight" means that which allows an intrinsic viscosity exceeding 2 as measured by the method described later.

### CONVENTIONAL TECHNOLOGY

Polyamides represented by nylon 6 and nylon 66 have been widely used in the form of moldings such as fibers, plastics, films, etc. In recent years, such moldings have been required to have an improved tensile strength and toughness; as a result, high-molecular-weight moldings are highly demanded. Yet, for obtaining high-molecular-weight moldings, conventionally, chips already having a high molecular weight are melted in a kneader and molded. However, in this case, in re-melting, molecular weight lowering and a decomposition reaction of the terminal groups may occur. Also, for making chips with a high molecular weight, a polycondensation reaction at a high temperature for an extended period in a nitrogen atmosphere or in vacuum may be needed. In such cases, due to mechanical difficulties such as stirring, etc., there is a limit on the molecular weight of the polymers that can be achieved. In another method, polymers having a molecular weight elevated to a certain level are subjected to solid-state polymerization. In this case, a long reaction time is required, resulting in poor productivity with difficulties in the suppression of side reactions.

On the other hand, for obtaining polyamides with a high degree of polymerization, in British Patent No. 693645, the bis-N-acyllactam type of chain extenders are added during the polymerization of polyamides; in Japanese Kokai Patent No. Sho 61[1986]-171732, carbamoyllactam-type chain extenders are added to polyamides and reacted in an extruder. However, in the former method, there are still problems of mechanical stirring difficulties and molecular weight lowering during re-melting as described above, and in the latter method the polymers obtained have an intrinsic viscosity of only 1.8, which is low, thus they are not satisfactory.

To overcome such problems, we had proposed a method involving the reaction of a polyamide with a difunctional N-acyllactam in an extruder (Japanese Kokoku Patent No. Sho 57[1982]-53169), enabling a super-high molecular weight to be easily achieved. However, according to further study, it became apparent that in the moldings obtained from such polymers,

melting is not sufficient, so the moldings contain a large amount of unreacted lactam monomers, which remains as a problem yet to be resolved.

## OBJECTIVE OF THE INVENTION

It is the objective of the present invention to provide a method for obtaining a polyamide molding with low melting-point lowering and a low lactam monomer content, without requiring a polymerization process involving a complicated operation, and yielding only a limited elevation of the molecular weight.

## CONSTITUTION OF THE INVENTION

As a result of an intense investigation for achieving such an objective, we have discovered that when a difunctional N-acyllactam compound which is a chain extender, is kneaded with a polyamide that has a relatively low content of terminal amino group content in a specific relationship with the terminal carboxy group content, a super-high-molecular-weight polyamide molding having good physical properties with a low lactam monomer content and low melting-point lowering can be obtained. Thus, the present invention was attained.

Namely, the present invention concerns a method for the manufacture of a super-high-molecular-weight nylon 6 molding, characterized by the molding, in the desired shape, of nylon 6 of formulas (1) and (2) shown below, while being reacted with a difunctional N-acyllactam in a melt kneader:

$$\begin{array}{ll} C_{NH_2} - C_{COOH} > 20 & \dots \dots (1) \\ C_{NH_2} < 85 & \dots \dots (2) \end{array}$$

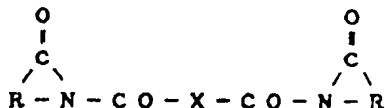
( $C_{NH_2}$  and  $C_{COOH}$  respectively represent the terminal amino group and terminal carboxy group amounts in the units of g-equivalents/ $10^6$  g).

In the present invention, the nylon 6 is a linear polymer obtained by polymerizing  $\epsilon$ -caprolactam. Within a range having no adverse effects on the fundamental properties of nylon 6, the  $\epsilon$ -caprolactam may be copolymerized with other monomers or blended. Here, in making nylon 6 having a terminal amino group content larger than the terminal carboxy group content, it is necessary to polymerize  $\epsilon$ -caprolactam with the addition of a small amount of an amine component. In this case, the amine component may be a monoamine, while using a diamine is advantageous in terms of the polymerization speed. The diamines may be aliphatic diamines such as hexamethylenediamine, m-xylylenediamine, etc.; aromatic diamines such as p-phenylenediamine, m-phenylenediamine, etc.; while any thermally stable diamines can be used.

Here, the most important factor needed for the polymers is the terminal group content, and it is essential to satisfy formulas (1) and (2) described above. If formula (1) is not satisfied, the final high intrinsic viscosity (hereafter referred to as  $[\eta]$ ) is not attained. If formula (2) is not

satisfied, even though formula (1) is satisfied, the melting point of the molding is low and an increased  $[\eta]$  cannot be expected.

The difunctional N-acyllactams that can be used in the present invention can be represented by the general formula below:



(X represents an alkyl or aromatic moiety; R represents an alkyl group).

Specific examples of the compounds represented by the general formula above include N,N'-terephthaloylbis- $\epsilon$ -caprolactam, N,N'-isophthaloylbis- $\epsilon$ -caprolactam, N,N'-adipoylbis- $\epsilon$ -caprolactam, N,N'-adipoylbis- $\epsilon$ -valerolactam, N,N'-isophthaloylbisvalerolactam, N,N'-isophthaloylbisbutyrolactam, N,N'-terephthaloylbisbutyrolactam, etc. Such compounds can be easily synthesized by reacting the corresponding carboxylic dihalides with lactams in the presence of an amine or an inorganic alkali such as KOH, etc.

In the present invention, in reacting polyamides of formulas (1) and (2) described above with the difunctional N-acyllactams, the nylon 6 chips are dry-blended with the lactam first, then melt-kneaded, or a difunctional N-acyllactam dissolved in  $\epsilon$ -caprolactam, etc.; is metered into the extruder inlet. The amount of the difunctional N-acyllactam added to the nylon 6 varies depending on the target molecular weight, while to obtain a high molecular weight, it should be approximately equivalent to the terminal amino group amount of the polymer. If it exceeds the equivalent amount, the molecular weight decreases with a large melting-point lowering with a high monomer content, thus it is not favored in terms of physical properties of the resulting moldings.

The melting temperature should be 10-150°C (preferably 50-80°C) higher than the melting point of the nylon 6, and the kneading time should be 1-20 min, preferably 2-6 min.

#### ACTION AND EFFECTS OF THE INVENTION

The present invention is characterized in that in enhancing the molecular weight of nylon 6 using the difunctional N-acyllactams, which are chain extenders, the terminal amino group content ( $C_{\text{NH}_2}$ ) of the polymer should be below 85 g-equivalents/ $10^6$  g, with the difference between the terminal amino group content and terminal carboxy group content ( $C_{\text{NH}_2} - C_{\text{COOH}}$ ) being above 20 g-equivalents/ $10^6$  g. If this difference is less than 20 g-equivalents/ $10^6$  g, even when the initial  $[\eta]$  is high, the  $[\eta]$  of the final moldings obtained by reacting with the N-acyllactams is not very high. Even when the difference is above 20, if the terminal amino group content is above 85 g-equivalents/ $10^6$  g, the resulting moldings would have a low melting point with a high lactam monomer content; in this case, a large amount (equivalent to the terminal

amino group amount) of N-acyllactam is needed, which is not advantageous in terms of economics and leads to uneven blending in the pellets. This also causes an unstable molding state (uneven thickness in parison in blow molding), dimensional unevenness of the final moldings, and problems of unstable production.

According to the present invention, pellets, fibers, films, and injection moldings of super-high- $[\eta]$  polyamides can be easily obtained, which have been difficult to obtain in conventional technology, and novel properties can be derived.

For example, as illustrated in Application Examples 12 and 13 described later, the Izod impact strength (notched) of the super-high- $[\eta]$  nylon 6 obtained by the present invention is up to 2.5 times that of conventional products, thus new applications are expected.

## APPLICATION EXAMPLES

Next, application examples are illustrated, while the present invention is not limited to such examples.

## DEFINITIONS OF TEST AND MEASUREMENT METHODS

### a. Intrinsic viscosity $[\eta]$

A polymer (0.2 g, 0.4 g, 0.8 g) is dissolved in 100 mL of m-cresol and analyzed for  $\eta_{rel}$  ( $t/t_0$ ) at 35°C. Next,  $\eta_{rel} - 1/C$  is plotted with respect to each concentration  $C$  (g/100 mL), and  $[\eta]$  is obtained from the intercept of the straight line from three points.

The relationship between the  $\eta_{rel}$  obtained in sulfuric acid and the intrinsic viscosity  $[\eta]$  is represented by  $[\eta] = 0.56\eta_{rel} - 0.26$ . For example,  $\eta_{rel} = 3.62$  in Japanese Kokai Patent No. Sho 61[1986]-171732, as shown in Application Example 2, corresponds to  $[\eta] = 1.77$ .

### b. Terminal group contents

The terminal group content  $C_{NH_2}$  is obtained by dissolving the polymer in m-cresol and titrating with 0.01N p-toluenesulfonic acid. The  $C_{COOH}$  value is obtained by dissolving the polymer in benzyl alcohol and titrating with 0.1N sodium hydroxide.

### c. Injection molding

Test specimens are prepared using the Toshiba IS60B at the molding temperature of 260°C, die temperature of 60°C, and molding cycle of 40 sec.

### d. Evaluation of molding properties

Tensile strength according to ASTM D638

Bending strength according to ASTM D710

Izod impact strength according to ASTM D256.

## APPLICATION EXAMPLES 1-9, COMPARATIVE EXAMPLES 1-6

$\epsilon$ -Caprolactam was treated with m-xylylenediamine (MXD), melt-polymerized, washed with hot water, and dried to obtain nylon chips with a water content of 0.01-0.03%, monomer content of 0.20-0.30%, and various terminal group contents (see Table I). The base chips obtained were dry-blended with N,N'-terephthaloylbiscaprolactam in an amount equivalent to the terminal amino groups, melt-kneaded in an extruder at 270°C for 4 min, extrusion-molded, and cut to obtain pellets. The results are summarized in Table I. It is learned that when the polymers made of excess terminal amino groups according to the present invention are used as base chips, super-high- $[\eta]$  nylon 6 moldings with melting points above 218°C and monomer content below 1% are obtained.

Table I

	Base chips				TL addition amount		Molding pellets				
	MXD <sup>a</sup> (mol%)	$[\eta]$	C <sub>NH2</sub>	C <sub>COOH</sub>	(wt%)	g-equivalents / 10 <sup>6</sup> g	$[\eta]$	C <sub>NH2</sub>	C <sub>COOH</sub>	Melting point	Monomer content
Comparative Example 1	0	1.34	45	48	0.80	45	1.80	4	50	221	0.60
Comparative Example 2	0	1.85	30	31	0.54	30	1.98	6	39	221	0.42
Comparative Example 3	0.05	1.60	40	29	0.71	40	1.95	6	41	220	0.50
Application Example 1	0.10	1.60	45	25	0.80	45	2.68	6	34	219	0.60
Application Example 2	0.20	1.62	56	13	1.00	57	4.00	3	18	219	0.71
Application Example 3	0.25	1.46	65	13	1.16	65	4.07	4	19	219	0.75
Application Example 4	0.30	1.36	75	12	1.34	75	3.95	3	18	218	0.80
Application Example 5	0.35	1.25	85	12	1.50	85	3.80	3	20	218	0.89
Comparative Example 6	0.40	1.16	95	12	1.69	95	3.18	6	23	216	0.25
Comparative Example 7	0.50	1.00	110	13	1.96	110	2.96	5	22	215	0.40
Comparative Example 8	1.00	0.66	175	10	3.13	176	2.50	7	35	214	2.00
Comparative Example 9	0.20	1.62	56	13	0	0	1.60	56	14	221	0.30

a) MXD: m-xylylenediamine

b) TL: N,N'-terephthaloylbis- $\epsilon$ -caprolactam

c) Value after melt kneading at 260°C x 4 min

Comparative Example 6 corresponds to Application Example 1 of Japanese Kokoku Patent No. Sho 57[1982]-53169 described above. Also, in Application Example 7 of the above patent specification, the terminal amino group content was erroneously given as 46.1 equivalent/g, but the correct value is 96.1. In Application Example 7, using the same parameters as Application Example 1 is obvious with respect to  $[\eta]$  and the molecular weight. The terminal groups and molecular weights are in a certain relationship, and when  $[\eta]$  is 1.15, the terminal group amount is that of Application Example 1, which was confirmed by our experiments.

	NH <sub>2</sub>	COOH	[ $\eta$ ]	Molecular weight
Application Example 1	96.1	12.6	1.15	$1.8 \cdot 10^4$
Application Example 7	46.1	12.6	1.15	$1.8 \cdot 10^4$

#### APPLICATION EXAMPLE 10

$\epsilon$ -Caprolactam was treated with 0.2% of hexamethylenediamine in place of m-xylylenediamine, melt-polymerized, washed with hot water, and dried to obtain nylon 6 chips with  $[\eta] = 1.60$ ,  $C_{\text{NH}_2} = 57$ ,  $C_{\text{COOH}} = 14$ . The chips were dry-blended with 0.96 wt% (57 g-equivalents) of N,N'-adipoylbis- $\epsilon$ -caprolactam and pelletized similarly as in Application Examples 1-5 to obtain pellets with  $[\eta] = 3.96$ ,  $C_{\text{NH}_2} = 4$ ,  $C_{\text{COOH}} = 17$ , melting point of 219°C, and monomer content of 0.65%.

#### APPLICATION EXAMPLE 11

As in Application Example 10, 1.00 wt% (57 g-equivalents) of N,N'-terephthaloylbis- $\epsilon$ -caprolactam was used with respect to the polymer in place of the N,N'-adipoylbis- $\epsilon$ -caprolactam to obtain pellets with  $[\eta] = 3.79$ ,  $C_{\text{NH}_2} = 7$ ,  $C_{\text{COOH}} = 17$ , melting point of 218°C, and monomer content of 0.68%.

#### APPLICATION EXAMPLES 12 AND 13, COMPARATIVE EXAMPLE 10

The base chips used in Application Example 2 were dry blended with designated amounts of N,N'-terephthaloylbis- $\epsilon$ -caprolactam and injection molded to obtain test specimens with the properties shown in Table II. By the super-high  $[\eta]$ , the notched impact strength is increased greatly.



Table II

	Application Example 12	Application Example 13	Comparative Example 10
Base chips [h]	1.62	1.62	1.65
C <sub>NH2</sub>	56	56	35
C <sub>COOH</sub>	13	13	37
Amount of N,N'-terephthaloylbis- $\epsilon$ -caprolactam added	1.00 (56 g-equivalents)	0.79 (44 g-equivalents)	0
Molded polymer properties [h]	3.80	2.83	1.56
C <sub>NH2</sub>	6	11	31
C <sub>COOH</sub>	18	17	38
Melting point (°C)	218	219	222
Monomer content (%)	0.68	0.45	0.10
Molding properties			
Tensile strength (kg/cm <sup>2</sup> )	660	660	680
Bending strength (kg/cm <sup>2</sup> )	910	920	960
Bending modulus (kg/cm <sup>2</sup> )	23100	23500	24600
Notch impact strength (kgcm/cm)	17.6	12.0	6.8

## APPLICATION EXAMPLE 14

The base chips used in Application Example 2 were dry blended with 1.00 wt% (107 g-equivalents) of N,N'-terephthaloylbis- $\epsilon$ -caprolactam, 0.018 wt% of cuprous iodide, and 0.24 wt% of potassium iodide, then extruded using a 22 mm  $\phi$  extruder-type spinneret at a cylinder temperature of 280°C, pack temperature of 305°C, extrusion rate of 10 g/min (dwell time of about 6 min), and spinning speed of 250 m through 12 orifices, wound, then drawn at a draw ratio of 3.5 on a hot plate at 190°C to obtain a fiber of  $[\eta] = 2.75$ , C<sub>NH2</sub> = 7, C<sub>COOH</sub> = 34, tenacity = 9.0 g/de, and elongation = 16%.

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